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THE ADSORPTION OF N ATOMS ON Pt(110) AND Cu(111) SURFACES

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Abstract

Large quantities of nitrogen adsorb after the gas is atomized by a high-frequency discharge on both surfaces. The total coverages reached a half monolayer with respect to the surface metal atoms. An ordered LEED pattern was not observed during the adsorption on Cu(111). A small amount of adsorbed N ( $2 \times 10^{14}$  atom/cm<sup>2</sup>), however, produced a (2x2) LEED pattern on Pt. A larger quantity of adsorbed N, similarly to the adsorption of CO, induced a (1x2)-(1x1) change in the periodicity of the reconstructed Pt surface. Nitrogen desorbed from Cu(111) surfaces in two stages, with one peak maximum which shifted from 620 to 700 K with increasing coverage ( $\beta_1$  state), and with another peak at 773 K ( $\beta_2$  state). Activation energies for desorption were 29, and 36 kcal/mol. Nitrogen desorbs from Pt(110) in only one stage, with a peak at 445 K. The activation energy is 25 kcal/mol.

Introduction

We recently investigated the interactions of isocyanic acid with Pt(110) and Cu(111) surfaces by means of LEED, Auger and thermal desorption mass spectrometry [1,2]. In order to facilitate the interpretation of the results, it seemed necessary to know more about the nature of the adsorbed N atom on these surfaces, and its surface interaction with CO. The adsorption of activated nitrogen on Pt(111), (100) and stepped surfaces was recently investigated by Schwaha and Bechtold [3]. Activated nitrogen was adsorbed at 300 K on all three surfaces up to about half the monolayer coverage. No additional LEED patterns indicative of any long-range order of adsorption were observed.

Experimental

Experiments were carried out in a stainless steel UHV chamber equipped with a 4-grid retarding field analyzer for low-energy electron diffraction (LEED) and for Auger analysis, with a quadrupole mass analyzer to monitor gas-phase composition and with several gas inlets. The vacuum system was evacuated with ion pumps and a titanium getter. A base pressure of  $1.5 \times 10^{-10}$  Torr was reached.

The Pt(110) crystal was cut from a single-crystal rod of ultrahigh-purity platinum (5 N) obtained from Materials Research Corporation. The sample was cleaned by heating at 1300 K for several hours, followed by argon ion bombardment. The remaining carbon was removed in a brief reaction with oxygen at 900 K. Finally, the sample was annealed at 1300 K. The clean an-

nealed surface was characterized by a (1x2) LEED pattern. The Cu(111) crystal and its cleaning procedures were the same as used in the study of the adsorption of H<sub>2</sub>CO [1]. Nitrogen atoms were generated by activating N<sub>2</sub> with a high-frequency discharge, similarly as described by Schwaha and Bechtold [3].

## Results and Discussion

### 1. Pt(110) Surface. Auger and LEED Studies

Exposure of Pt(110) surface to N<sub>2</sub> up to 180 L at 300-473 K caused no change in the Auger spectrum. An increase in the Auger signal at approximately 380 eV, due to adsorbed nitrogen, was observed, however, when the nitrogen was activated. As the signals of N (380 eV) and Pt (382 eV) can not be separated, the relative N signal,  $N_{380} + Pt_{382}/Pt_{238}$ , was used to follow the adsorption of nitrogen. In Fig. 1 this value has been plotted against the exposure. Approximate saturation was reached at about 100-150 L (N+N<sub>2</sub>). This corresponds to a surface concentration of  $8 \times 10^{14}$  N atom/cm<sup>2</sup>. This value was calculated by using the correlation between the relative N signal and the surface concentration of adsorbed N atoms determined by Gland and Korchak [4]. The clean annealed surface gave a (1x2) LEED pattern. Exposure of this surface to 5 L (N+N<sub>2</sub>) ( $2 \times 10^{14}$  N atom/cm<sup>2</sup>) produced a weak additional (2x2) LEED pattern with a diffuse background. Further exposure caused a reordering of the surface Pt atoms from the (1x2) to the (1x1) structure.

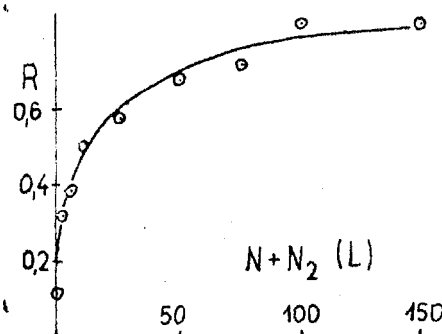


Fig. 1 - Relative N signal versus nitrogen exposure on Pt(110).

### Thermal Desorption Measurements

In order to eliminate the contribution of CO (28 amu) from the residual gas, thermal desorption measurements were carried out using labelled nitrogen, N<sub>2</sub><sup>30</sup>. Thermal desorption spectra were taken at a linear heating rate of 13 K sec<sup>-1</sup> by following the change in the 30 amu signal. The results are shown in Fig. 2. At low coverage, up to  $\theta \sim 0.25$ , the maximum temperature of the peak was shifted to lower temperature with the increase of the coverage. The peaks were not symmetrical; on the high-temperature side two shoulders were observed. In the range  $\theta = 0.25-1$ , the desorption process seemed to be of first order. When the 28 amu signal was followed, a second stage, at 493-513 K, was also observed, caused by the desorption of CO. This CO very probably desorbed from the walls of the vessel during the discharge, and readsorbed on the Pt surfaces. This phenomenon was previously observed [3]. From the intensity changes in the 14 amu signal, we obtained the same desorption spectrum as in the measurement of the 30 amu

signal. The kinetic parameters of the desorption process were determined with variation of the heating rate. We obtained 25 kcal/mol for the activation energy, and  $1 \times 10^{12} \text{ s}^{-1}$  for pre-exponential factor.

## 2. Cu(111) Surface. Auger and LEED Studies

The adsorption of atomic N was previously studied only on a Cu(100) surface. The nature of the surface interaction was established by LEED, Auger, UPS and XPS methods [5]. Exposure of the clean surface to activated nitrogen at 300 K led to the appearance of a nitrogen signal at 380 eV. An important observation was that no signal due to surface carbon was detected, even at the high nitrogen exposure. The surface coverage of nitrogen was calculated in the manner described earlier [6]. Saturation coverage was reached at about half the monolayer. The adsorption of activated nitrogen produced no additional diffraction spots on the LEED pattern of the clean Cu(111) surface. An increase of the diffuse background was observed.

### Thermal Desorption Measurements

Thermal desorption spectra were taken by following the change in the 28 amu signal (Fig. 3). Nitrogen desorbed from the Cu(111) surface in two stages. The low-temperature stage is designated by  $\beta_1$ , and the high-temperature one by  $\beta_2$ . TPD spectra taken at different coverages show that the  $\beta_2$  sites begin to be populated first, but are filled up very soon (Fig. 3). A much greater amount of adsorbed nitrogen is bonded to the  $\beta_1$  sites. The peak temperature of the stage, 773 K, is practically independent of the coverage, indicating that the desorption of nitrogen in this stage follows a first-order rate law. The maximum temperature of the  $\beta_1$  peak was shifted from 620 K to 700 K with the increase of the coverage. Similar spectra and behaviour were found when labelled nitrogen,  $\text{N}_2^{20}$ , was used, or

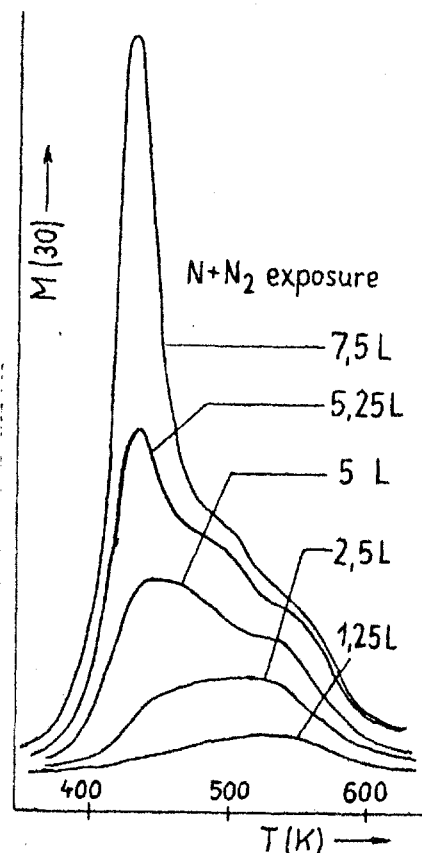


Fig. 2 - TD spectra of nitrogen from Pt (110).

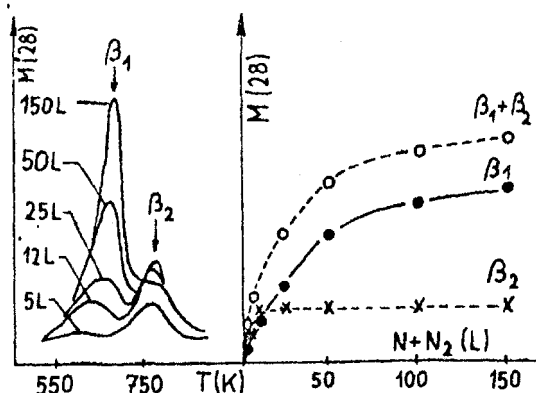


Fig. 3 - TD spectra of  $\text{N}_2$  from Cu(111) and the amount of desorbed  $\text{N}_2$  versus exposure.

when the intensity of the 14 amu signal (singly charged  $N^+$ ) was followed. This shows that CO desorbing from the wall during the activation of nitrogen did not contaminate the surface, and hence did not influence the TPD spectrum. This is in harmony with previous measurements, i.e. no detectable adsorption of CO occurs on the Cu(111) surface at 300 K [7]. The amounts of  $N_2$  desorbed in the two stages were calculated by careful integration of the areas of the peaks. These values showed the same dependence on the nitrogen exposure (Fig. 3) as the relative N signal. In harmony with this, the intensity of the relative N signal increased linearly with the increase of the sum of the areas of the nitrogen desorption peaks. The activation energies for the desorption of nitrogen, calculated in a similar way as in the case of Pt, were 29 and 36 kcal.

The characteristics of the thermal desorption of  $N_2$  from Pt (110) and Cu(111) agree well with those observed after the adsorption of HNCO on these samples [1,2]. This result supports the explanation proposed for the behaviour of NCO species on these surfaces. We mention here, that accurate determination of the ratio of the signals at 28 and 14 amu indicate that nitrogen atoms recombine before desorption from both surfaces.

#### The Surface Interaction of Atomic N with CO

Some measurements were carried out concerning the surface interaction of atomic N and CO on Pt(110) surface. In these experiments  $N_2(30)$  was used. When the surface was dosed, first with CO (to saturation) and then with activated N, the low-temperature peak at 420 K for the thermal desorption of CO was transformed into a new peak, with  $T_{max} = 458$  K. No change occurred in the high-temperature peak of CO desorption. From determination of the amount of CO desorbed, it appeared that less than 20% of the adsorbed CO was displaced from the surface by activated N. On the other hand, the desorbing nitrogen showed that on the CO-covered surface 90% of the quantity required for monolayer coverage was adsorbed. This may indicate that the Pt surface was not covered completely with CO. When the dosing sequence was reversed similar results were obtained. UPS measurements are in progress to establish whether NCO species is formed in the surface interaction of adsorbed N with CO at low-temperatures.

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